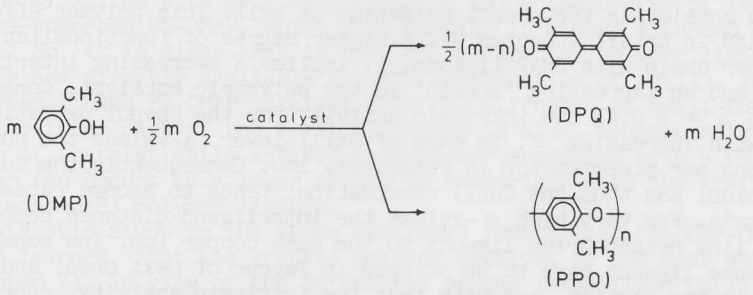
SUMMARY

This thesis describes the results of an investigation on the catalysis of the oxidative coupling of 2,6-dimethylphenol (DMP) by Cu(II) complexes of polystyrene-bound dimethylamino pyridine (PS-DMAP). In this process the reaction products are the C-C coupled product 'diphenoquinone (DPQ)' and the C-O coupled product 'polyphenyleneoxide (PPO)', an engineering plastic.



DMAP based Cu(II) complexes proved to be very active and specific catalysts for the formation of the commercially interesting PPO. The oxidation of DMP implies a reduction of Cu(II) complexes to Cu(I) complexes. Subsequently Cu(I) is reoxidized to Cu(II) by molecular dioxygen and the redox cycle can be repeated.

In order to be able to trace possible rate enhancing effects of the polymer chain on the redox process, the catalysis by Cu(II) complexes of the low molar mass analogue DMAP was studied first (Chapter 2). A detailed spectroscopic investigation (UV/Vis, EPR, X-Ray) revealed, that an equilibrium exists between dinuclear and mononuclear Cu(II)-DMAP complexes under catalytic conditions. Further, DMAP (= L) was found to coordinate to Cu(II) through the pyridine N-atom. An increase of the ratio L/Cu enhances the amount of mononuclear complexes $Cu(II)L_4(OH)Cl$ as well as the catalytic activity and specificity (maximum 97% of PPO). In case of the low molar mass catalyst the Cu(I) reoxidation proved to be the rate-determining step in the redox cycle. The rate of this Cu(I) reoxidation proved to be second order in copper. It was concluded, that the complexes $Cu(II)L_4(OH)Cl$ are active in the phenol oxidation, whereas the reoxidation reaction demands dimerization of the generated mononuclear Cu(I) complexes.

The yield of the monomer 4-(N-methyl-N-p-vinylbenzylamino)pyridine, which can be converted into PS-DMAP by radical copolymerization with styrene, was considerably improved with respect to the synthesis and the purification procedure described in the literature (Chapter 3). A study on the complex structures of Cu(II)-PS-DMAP in solution learned that these are similar to those of the low molar mass analogue. An important point of difference, however, is the so called 'polydentate effect', which for comparable values of L/Cu leads to a more complete formation of the catalytically active $Cu(II)L_4(OH)Cl$ and which yields more stable complexes. Under standard conditions the polymeric catalyst proved to be five times as active as its low molar mass analogue. It became clear that the Cu(I) reoxidation has been accelerated in such a way that now the oxidation of DMP, for which Michaelis-Menten kinetics in terms of substrate proved to be valid, is the rate-determining step in the redox cycle. The explanation is based upon the high local copper concentration in the polymer coils, which can be regarded

as separate microreactors in the applied region of polymer concentration. The high local copper concentration accelerates the Cu(I) dimerization and, consequently, the Cu(I) reoxidation significantly. Further the nonpolar polymer backbone would accelerate the reoxidation of Cu(I) as well (Tsuchida). In case of the polymeric catalyst the rate-determining step, i.e. the phenol oxidation, is also accelerated. In the first place by the above mentioned relatively large amount of $Cu(II)L_{II}(OH)Cl$ due to the polydentate effect. Further an 'entropic strain', present in the polymeric catalyst, proved to accelerate the phenol oxidation as well. This polymer effect was studied in detail (Chapter 4). A higher degree of functionalization of the polymer chain with DMAP ligands, α, implies a decreasing interligand distance and an increasing 'strain' in the polymeric catalyst. Consequently, for $0.096 \lesssim \alpha \lesssim 0.23$ the intrinsic activity for the phenol oxidation increases with increasing α. In case of still lower α-values the number of copper ions per microreactor is relatively low. Consequently the Cu(I) dimerization, and thus the Cu(I) reoxidation, tends to become rate-determining again. For very high α-values the interligand distance becomes too small to link neighbouring ligands to the same copper ion. The consequence is that some ligands have to be skipped in favour of next ones, and the 'strain' in the complex, and with that the intrinsic activity, decreases. The catalytic specificity proved to be independent of α. Moreover, it proved to equal that of the low molar mass catalyst. This was interpreted as an indication that the formation of the products takes place in solution and not in the complexes.

In Chapter 5 a mechanism of the oxidation of DMP is presented, which is consistent with all catalytic and spectroscopic results in Chapters 2, 3 and 4 and with recent results of related work and generally accepted steps in the oxidative coupling of phenols. The validity of a second order in copper for the Cu(I) reoxidation was confirmed once more and convincing evidence was obtained for a first order dependence on the copper concentration of the phenol-oxidation rate. This last mentioned result came to light by changing the number of copper ions per microreactor and measuring the resulting catalytic activity. It had already been mentioned that the phenol oxidation obeys Michaelis-Menten kinetics in DMP. In a relatively fast equilibrium phenolate anion replaces OH^- in the mononuclear Cu(II)-DMAP complex and water is formed. In a subsequent step, which is rate-determining for the polymeric catalyst, an electron is transferred from the phenolate anion to the Cu(II) ion, which is transformed into a Cu(I) ion. At the same time phenolate is transformed into a phenoxy radical. It could be made plausible that this phenoxy radical remains coordinated in the Cu(I) complex. For the Cu(I) reoxidation an equilibrium is suggested in which molecular dioxygen is reversibly bound to mononuclear Cu(I)-DMAP complexes, prior to dimerization of the formed adducts with dioxygen-free Cu(I)-DMAP complexes. This dimerization is rate-determining in case of the low molar mass catalyst. Dioxygen-bridged dimers are generated. After two subsequent 2-electron transfers to dioxygen, the first one from both Cu(I) ions and the second one from both phenoxy radicals via both Cu(II) ions, two phenoxonium ions have been generated. These phenoxonium ions leave the complex, take part in the product formation in solution, the dimeric complex falls apart into two mononuclear Cu(II) complexes and the cycle can be repeated.

In Chapter 6 a qualitative spectroscopic investigation on the structure of immobilized Cu(II)-PS-DMAP complexes is described. The used immobilization techniques were grafting and partial adsorption on silica, and crosslinking with 2% divinylbenzene. The formation of catalytically active com-

complexes Cu(II)L_4(OH)Cl proved to be most complete in case of the silica-grafted polymeric ligands. This could be explained by the more extended conformation of the immobilized grafted coils with respect to the partially adsorbed PS-DMAP chains. In case of adsorbed PS-DMAP the number of hydrogen-bridges between the basic DMAP's and the acidic SiOH's of the silica particles is relatively high, because no silanol groups were lost due to modification reactions as met in the grafting-procedure. Further the degree of loading of silica with grafted polymer is twice the degree of loading of the silica-adsorbed PS-DMAP, which also results in a more extended conformation. So, it is clear that in case of the grafted polymer ligands more DMAP units are directly available for the coordination of Cu(II). In case of the cross-linked PS-DMAP catalyst even the diffusion of small Cu(II) ions to the inner part of the resin particles is slow. Consequently, the formation of (catalytically active) mononuclear complexes with 4 DMAP's per copper ion occurs to a lower extent in comparison with the grafted (and even the adsorbed) polymer ligands.

A catalytic study on the above mentioned immobilized PS-DMAP-Cu(II) complexes learned, that the grafted polymer catalyst is the most active one (Chapter 7). In view of the structures of the immobilized Cu(II)-PS-DMAP complexes (Chapter 6) this was to be expected. However, under standard conditions the grafted catalyst is six times less active than comparable unbound PS-DMAP-Cu(II) catalysts.

Application of all types of immobilized PS-DMAP-Cu(II) catalysts in a continuous stirred tank reactor (CSTR) for the oxidative coupling of phenols showed a drastic decrease of phenol conversion in time. The mentioned catalysts proved to be destroyed by hydroxide, generated by reaction of produced water with the strongly basic DMAP's. In agreement a catalyst based upon the less basic poly(styrene-co-4-vinylpyridine) adsorbed on to silica proved to yield an invariable phenol conversion in the CSTR for at least 230 h.